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Family list
20 family members for:
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1   NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS
Publication info: **AT201661T T** - 2001-06-15

2   Niobium and tantalum pentoxide compounds
Publication info: **AU714039B B2** - 1999-12-16

3   Niobium and tantalum pentoxide compounds
Publication info: **AU7515296 A** - 1997-04-30

4   NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS
Publication info: **CA2234672 A1** - 1997-04-17

5   Niobium and tantalum pentoxide compounds
Publication info: **CN1106347C C** - 2003-04-23
                  CN1203567 A - 1998-12-30

6   Method of preparing electron tube metallic oxide precusor
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7   NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS
Publication info: **DE69613135D D1** - 2001-07-05

8   NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS
Publication info: **DE69613135T T2** - 2002-03-07

9   NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS
Publication info: **EP0854841 A1** - 1998-07-29
                  EP0854841 B1 - 2001-05-30

10   A PROCESS OF PRODUCING VALVE METAL OXIDES OR HYDRATES
THEREOF, AND NIOBIUM PENTOXIDE TANTALUM PENTOXIDE
POWDERS
Publication info: **HK1017661 A1** - 2003-08-29

11   PROCESS FOR PRODUCING NIOBIUM AND TANTALUM PENTOXIDE
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Publication info: **IL124046 A** - 2001-10-31

12   COMPOUNDS OF TANTALUM PENTOXIDE AND NIOBIUM PENTOXIDE
Publication info: **RU2189359 C2** - 2002-09-20

13   Niobium and tantalum pentoxide compounds
Publication info: **TW425374B B** - 2001-03-11

14   Process for producing niobium and tantalum compounds
Publication info: **US6338832 B1** - 2002-01-15

15   Process for producing niobium and tantalum compounds
Publication info: **US6984370 B2** - 2006-01-10
                  US2003082097 A1 - 2003-05-01

16   Process for producing niobium and tantalum compounds
Publication info: **US2005232850 A1** - 2005-10-20

17   NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS
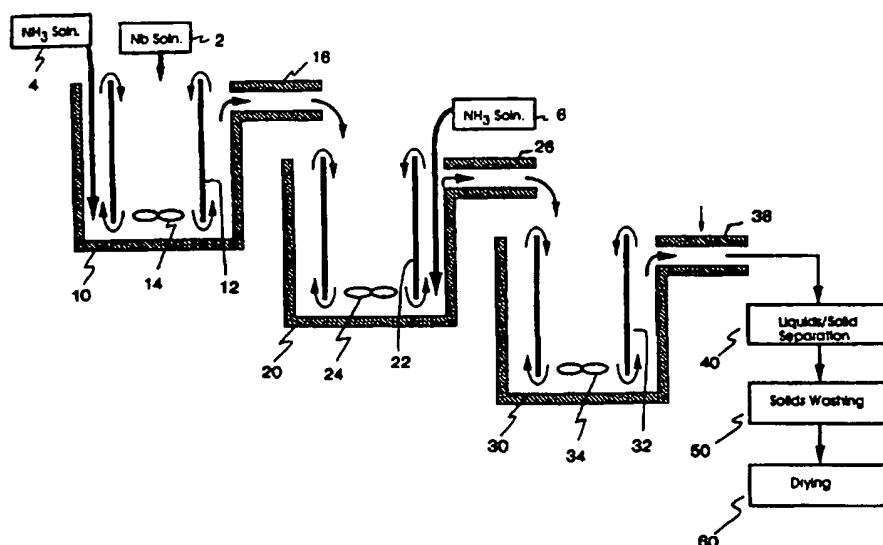Publication info: **WO9713724 A1** - 1997-04-17

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(54) Title: NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS

(57) Abstract

A process for producing valve metal oxides, such as tantalum pentoxide or niobium pentoxide with a narrow particle size distribution within a desired particle size range. Valve metal solution from digestion of valve metal material containing ore is processed under controlled temperature, pH, and residence time conditions to produce the valve metal pentoxide and pentoxide hydrates. Also, disclosed are new tantalum pentoxide and niobium pentoxide products and new tantalum pentoxide precursors and niobium pentoxide precursors.

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NIOBIUM AND TANTALUM PENTOXIDE COMPOUNDS

The present invention also relates to novel valve metal
compounds, in particular to novel niobium pentoxides, niobium
hydrates, tantalum pentoxides and tantalum hydrates and to
5   improved processes for producing such compounds.
BACKGROUND OF THE INVENTION

Valve metals are characterized by a protective oxide
surface layer that tends to protect the metal from corrosion and
include tantalum, niobium, aluminum, zirconium, tungsten,
10 titanium and hafnium. As used herein the term "valve metal"
refers to tantalum and niobium. A commercially valuable form of
"valve metal" is a valve metal oxide such as tantalum pentoxide
(Ta_2O_5) or niobium pentoxide (Nb_2O_5). Tantalum and niobium are
conventionally extracted from mineral ores with hydrofluoric
15 acid (HF) or mixtures of hydrofluoric acid and sulfuric acid
(HF/H_2SO_4) forming heptafluoro complexes which are typically
separated by solvent extraction, e.g. using methylisobutylketone
(MIBK), to provide an aqueous solution of a heptafluoro complex
of the valve metal. The valve metal pentoxide is precipitated
20 by treating the heptafluoro complex solution with ammonia and
recovered by filtration.

As disclosed in U.S. Patent 5,068,097 valve metal
pentoxides are commonly produced in a batch process. It is
believed that in conventional batch processes it is difficult to
25 control particle size and particle size distribution of valve
metal oxides because such precursors are precipitated over a
varying pH range as ammonia is added to the solution. The
addition of ammonia raises the pH of the solution; however, the
rise in pH occurs over time as the ammonia reacts with the
30 solution. It is believed that the precipitation of valve metal
pentoxide precursor begins at a first pH, continues as the pH
rises, and ends at a higher pH. The pH at which precipitation
actually occurs affects the particle size of the precipitates,
and thus it is believed that as precipitation occurs over a
35 range of pH's, different particle sizes are produced, thereby
increasing the particle size distribution of valve metal oxide
compounds. The precipitation over a wide range of pH in a batch

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process also makes it difficult to produce valve metal pentoxides of a particular particle size.

We have discovered that this problem can be overcome by the process of the present invention wherein a solvent-extracted,
5 valve metal heptafluoro complex, e.g. from HF digestion of valve metal-containing ore, is processed under controlled temperature, pH and residence time conditions.

SUMMARY OF THE INVENTION

This invention provides valve metal pentoxide precursor and
10 valve metal pentoxide of uniform particle size and narrow particle size distribution. In one aspect the invention provides valve metal pentoxide having large, dense, spherical agglomerates of particles, relatively low surface area and high bulk density characterized more particularly as tantalum
15 pentoxide having BET surface area less than 3 square meters per gram (m^2/g) and bulk density of at least 3 grams per cubic centimeter (g/cc) for Ta_2O_5 and as niobium pentoxide having BET less than 2 m^2/g and bulk density greater than 1.2 g/cc. Another aspect of the invention provides valve metal pentoxide
20 of fine particles with relatively high surface area and low bulk density characterized more particularly as tantalum pentoxide having BET surface area greater than 3 m^2/g and a bulk density less than 3 g/cc for and as niobium pentoxide having a BET surface area greater than 2 m^2/g and a bulk density less than
25 1.2 g/cc. This invention also provides a process for producing valve metal pentoxides, such as tantalum pentoxide or niobium pentoxide, with a narrow particle size distribution within a desired particle size range.

The present invention also provides a process for producing
30 valve metal oxides, such as tantalum pentoxide or niobium pentoxide. The process of the present invention may be advantageously utilized to produce valve metal pentoxides with a narrow particle size distribution within a desired particle size range. This process comprises reacting valve metal fluoro
35 complexes with ammonia under controlled temperature, pH and residence time conditions in a series of two or more stirred reactors to precipitate hydrated valve metal pentoxide precursor.

This invention also provides valve metal pentoxide precursor characterized by having a line broadened d-values under x-ray analysis of 6 ± 0.3, 3 ± 0.2 and 1.8 ± 0.1. Such precursor is a hydrated oxide which is also characterized as having a low fluoride content, e.g. less than 500 ppm.

BRIEF DESCRIPTION OF THE DRAWINGS:

Figure 1 illustrates a reactor system for carrying out a preferred process of the present invention.

Figures 2a, 2b, 2c and 2d are scanning electron microscope (SEM) photographs of a calcined niobium pentoxide powder of the present invention produced in the manner described in Example 3 below.

Figures 3a, 3b, 3c and 3d are SEM photographs of a calcined niobium pentoxide powder of the present invention produced in the manner described in Example 5 below.

Figures 4a, 4b, 4c and 4d are SEM photographs of a calcined tantalum pentoxide powder of the present invention produced in the manner described in Example 9 below.

Figures 5a, 5b, 5c and 5d are SEM photographs of a calcined tantalum pentoxide powder of the present invention produced in the manner described in Example 10 below.

DETAILED DESCRIPTION OF THE INVENTION:

This invention provides a novel and improved process for producing valve metal pentoxide comprising:

(a) providing in a first vessel a mixture of an ammonia solution and an aqueous solution comprising fluoride ion and valve metal-fluoro compound selected from the group consisting of fluorotantalic acid and niobium oxyfluoride at temperature, pH and residence time conditions to initiate precipitation of a hydrated valve metal pentoxide precursor;

(b) transferring said mixture into at least one other vessel for mixing at temperature, pH and residence time conditions to further precipitate a hydrated valve metal pentoxide precursor; and

(c) separating said hydrated valve metal pentoxide precursor from said mixture and converting said hydrated valve metal pentoxide precursor to valve metal pentoxide, e.g. by calcination.

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Product purity may be controlled by the purity of the valve
metal complex fed into the reactor system. Complexing agents,
such as ethylenediaminetetraacetic acid (EDTA) and the like, may
be added to the aqueous fluoro-solution to aid in retaining
5   impurities in solution.
        A preferred method for controlling the reaction
temperature, pH, and residence time is through the use of
continuous, stirred tank reactors, e.g. a cascading draft tube
reactor system, where the reaction between the valve metal
10   fluoro complex and ammonia is begun in a first reaction vessel
at a first pH and temperature, and then continues through one or
more additional reaction vessels which may be maintained at
different pH's and/or different temperatures. In this process
the first pH (in the first vessel) and the second pH (in the
15   second vessel) may be substantially the same or different, and
may be controlled independently. Where it is desired to further
control the second pH, the process may also include the
additional step of introducing a second ammonia solution into
the second vessel and mixing the second ammonia solution and the
20   first mixture to obtain the second mixture at the second pH and
to react the first mixture and the second ammonia solution to
continue precipitation of valve metal pentoxide precursor.
Although a first and a second reaction vessel have been
described, additional reaction vessels may be utilized to
25   further control the process. For example, two reaction vessels,
maintained at slightly different pH's could be substituted for
the first and/or the second vessel, thereby raising the total
number of reaction vessels to four or five. In a preferred
embodiment the process includes the additional step of
30   transferring the second mixture into a third vessel maintained
at a third temperature and further mixing the second mixture to
complete precipitation of hydrated valve metal pentoxide
precursor prior to converting the hydrated valve metal pentoxide
precursor to valve metal pentoxide.   A further advantage is
35   that the present invention provides a continuous process for
producing valve metal pentoxides with a narrow particle size
distribution within a desired particle size range.

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        The hydrated valve-metal pentoxide precursor will generally
comprise a valve-metal pentoxide hydrate. Conversion from
hydrated valve-metal pentoxide precursor to valve metal
pentoxide may be accomplished by calcining or by a hydrothermal
5   process. Hydrated tantalum-oxide precursors can be converted to
tantalum pentoxide by calcining at temperatures of at least 790°
C. Niobium-oxide precursors can be converted to niobium
pentoxide by calcining at temperatures of at least 650° C.
        The residence time for the reactions in each vessel may be
10 controlled by the rate at which solutions are introduced into
and transferred from the vessels. Control of the residence time
impacts particle size and density. Increased residence time
increases particle size and density. Temperature can also
impact particle size; higher temperatures tend to speed
15 precipitation reaction and generate finer particles.
        In the preferred methods of the present invention,
controlling the pH and temperature of each vessel allows the
production of valve metal pentoxides (e.g., tantalum or niobium
pentoxides), having desired particle sizes and narrow particle
20 size distributions to be produced. In the process of the
present invention pH may be controlled by controlling the
addition of ammonia. The first pH (the pH in the first vessel)
should be maintained at a level sufficient to initiate
precipitation of the tantalum or niobium pentoxide product.
25 Generally, the first pH should range from 6 to 9.5, preferably
from 7 to 8 for agglomerated particles. The second pH (the pH
in the second vessel) should most preferably be maintained at a
level sufficient to assure substantially complete precipitation
of the tantalum or niobium pentoxide precursor. Generally the
30 second pH should range from 8 to 9.5, preferably from 8 to 8.5.
        When the first pH in the first reaction vessel is towards the
acidic side, addition of the second ammonia solution in the
second vessel may be necessary to achieve the desired second pH.
        In a preferred three vessel embodiment of the process of the
35 present invention, no additional ammonia is added in the third
vessel, and the pH of the third vessel will be substantially the
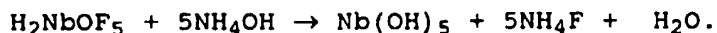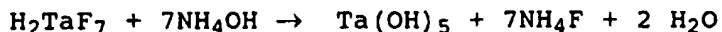same as, or slightly less than, the pH in the second vessel thus

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assuring that the precipitation reactions proceed to substantial
completion.

The choice of pH for each vessel will determine, in part,
the particle size of the pentoxide product produced by the
5   process. In general, the extremes of pH, i.e. near 6 and 9.5,
in the first vessel are advantageous for producing fine particle
sizes, with pH's in the middle of the range, i.e. near 7.5,
being advantageous for producing substantially spherical
(coarse) particle sizes.

10   As used herein, residence time refers to the time period in
which a reaction or reactions occur. Total or overall residence
time for the process is the sum of the residence time in each
reaction vessel. The minimum residence time for the process is
a residence time sufficient to precipitate valve metal pentoxide
15   precursor. The maximum residence time for the process will
generally be dictated by the desired product and the economics
of the process. In general, for given pH and temperature,
shorter total residence time is desirable for producing fine
particle size and longer total residence time is desirable for
20   producing coarse substantially spherical particle sizes. It is
also advantageous for the total residence time to be the
shortest time for a given temperature and pH which allows
substantially complete conversion of the valve metal-fluoro
compound to the desired hydrated valve metal pentoxide
25   precursor. As will be understood by those of ordinary skill in
the art, longer residence times may be achieved by recycling of
the solid phase.

Operating at elevated temperatures shifts the following
reactions to the right, thus promoting completion of the
30   reaction in the production of hydrated valve metal oxide
precursor:

$$H_2TaF_7 + 7NH_4OH \rightarrow Ta(OH)_5 + 7NH_4F + 2 H_2O$$

$$H_2NbOF_5 + 5NH_4OH \rightarrow Nb(OH)_5 + 5NH_4F + H_2O.$$

The temperature of the reaction vessels may be controlled by
35   conventional means including water jackets and the like.
Generally, for large scale production, the temperature of each
vessel will range from 40 to 95° C. For given pH and residence

time, higher temperature will produce finer particles and lower
temperature will produce coarser particles.

    For a two reactor system, the relationship between pH,
temperature and residence time, may be generally summarized as

5   follows:

Particle Size	Residence Time	Temperature	First pH	Second pH
Fine	Shorter	Higher	> 8 or < 7	8-9.5
Coarse	Longer	Lower	7-8	8-9.5

10 This table is provided by way of illustration only, and is not
meant, nor should be construed, to limit the scope of the
process of the present invention.

    With reference to Figure 1, there is shown a flow diagram
of a cascading draft tube reactor system suitable for carrying

15 out a preferred embodiment of the present invention comprising a
series of reaction vessels, with draft tubes, and circulation
(stirring) means. Such reaction vessels, draft tubes, and
circulation means suitable for use in the process of the present
invention are commercially known, and therefore are not

20 described in detail herein. Moreover, the process of the
present invention is not limited to being performed by
particular equipment, and may be performed by a wide variety of
different equipment suitable for carrying out the process steps
described above and below.

25   In a preferred process of the present invention, a valve
metal fluoro complex-containing solution 2, e.g. from digestion
and separation of a niobium containing ore, is added to the top
center of a first reaction vessel 10. The rate of addition of
the valve metal-containing solution 2 will depend on the size of

30 the reaction vessel, the desired residence time for the
reactions occurring in the vessel, and the rate at which the
first mixture is transferred out of the vessel. These variables
will be adjusted depending upon the type of particles desired.

    An ammonia solution 4 is added to the bottom outer

35 periphery of the first reaction vessel 10 outside the area
defined by draft tube 12. The rate of addition of the ammonia
solution 4 will also depend on the size of the reaction vessel,
the desired residence time for the reactions occurring in the

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vessel, and the rate at which the first mixture is transferred
out of the vessel. In addition, the rate of addition of the
ammonia solution 4 will depend on the desired pH of the first
mixture (pH_1) determined, in part, by the particle size desired
5   in the final product. Generally, pH_1 ranges from 6 to 9.5. For
a given temperature and residence time, pH_1 values near the
extremes of the range (near 6 or 9) will produce a finer
particle size in the final product while pH_1 values near the
center of the range (between 7 and 8) will produce a coarse
10 spherical particle size in the final product.

The first reaction vessel 10 is maintained at a first
temperature (T_1) determined, in part, by the desired particle
size of the final product. Generally, T_1 ranges from 30 to
95°C, and preferably from 50 to 70°C. For a given pH and
15 residence time, higher values for T_1 will result in final
product having finer particle sizes. Heat transfer means, e.g.
a water jacket, (not shown in Figure 1) may be utilized to
maintain the reaction vessels at desired temperature.

Circulation means 14, e.g. stirrer or pump, is utilized to
20 circulate and mix the valve metal-containing solution 2 and the
ammonia solution 4 within reaction vessel 10 to create a first
mixture. The direction of flow of the first mixture within the
first reaction vessel may be as shown by the arrows.
During circulation, a portion of the first mixture will exit the
25 first reaction vessel through conduit 16. The residence time
for the reaction occurring in the first reaction vessel, R_1,
may be controlled by varying the throughput rate, and/or the
size of the reactor and will determine, in part, the density of
the final product. For certain reactor sizes, R_1 can range from
30 about 2 minutes to 2 hours. For a given pH_1 and T_1, higher
values for R_1 will result in a final product having packed bulk
densities, e.g. of 1.2 g/cc or more.

The portion of the first mixture that exits the first
reaction vessel 10 through conduit 16 is introduced into the
35 inner periphery of a second reaction vessel 20 inside the area
defined by draft tube 22. The rate of addition of the first
mixture into the second reaction vessel 20 will depend on the
rate at which the first mixture is transferred out of the first

reaction vessel 10. An ammonia solution 6 is added to the outer
periphery and near the bottom of the second reaction vessel 20
outside the area defined by draft tube 22. The rate of addition
of the ammonia solution 6 will depend upon the size of the
5   second reaction vessel, the desired residence time for the
reactions occurring in the second reaction vessel, and the rate
at which the first mixture is transferred into the second
reaction vessel. In addition, the rate of addition of the
ammonia solution 6 will depend on the desired pH of the second
10   mixture (pH_2) determined, in part, by the desired particle size
of the final product. Generally, pH_2 ranges from 8 to 9.5,
depending upon the pH of the first reactor. For a given
temperature and residence time, the pH_2 value is selected to
assure complete reaction while limiting the amount of ammonia
15   consumed.

The second reaction vessel 20 is maintained at a second
temperature, T_2, determined, in part, by the desired density of
particles in the final product and the rate of reaction.
Generally, T_2 ranges from 30 to 95 °C, preferably 60 to 85 °C.
20   For a given pH and residence time, a higher value for T_2 will
result in final product with a finer particle size. Circulation
means 24 is used to circulate and mix the mixture entering the
second reaction vessel and the ammonia solution 6 within
reaction vessel 10 to create a second mixture. The direction of
25   flow of the second mixture within the second reaction vessel is
shown by the arrows. Reversal of flow can effect particle
characteristics depending on desired products.

During circulation, a portion of the second
mixture will exit the second reaction vessel through conduit 26.
30   The residence time for the reaction occurring in the second
reaction vessel, R_2, can be controlled by varying the
circulation rate and the size of the reactor and will determine,
in part, the completion of reaction within the second vessel.
To some degree it allows further precipitating and densification
35   of the particles. Thus, by varying R_2, different particle size
products may be produced. R_2 can range from 2 to 90 minutes.
For a given pH_2 and T_2, a higher value for R_2 will result in
final product having denser and coarser particles.

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The portion of the second mixture that exits the second
reaction vessel 20 through conduit 26 is introduced into the
inner periphery of a third reaction vessel 30 inside the area
defined by draft tube 32. The rate of addition of the second
5   mixture into the third reaction vessel 30 will depend on the
rate at which the second mixture is transferred out of the
second reaction vessel 20.

Circulation means 34 are utilized to circulate and continue
mixing of the second mixture in the third reaction vessel to
10   allow the precipitation of niobium pentoxide to proceed to
substantial completion. The direction of flow of the second
mixture within the third reaction vessel is shown by the arrows
but is not a limiting characteristic of the reaction. In cases
where no additional ammonia is added to the third reaction
15   vessel, the pH of the mixture in the third reaction vessel, pH_3,
will be slightly less than pH_2 depending upon the degree of
reaction completion in the third reaction vessel along with
ammonia volatilization rates.

The third reaction vessel 30 is maintained at a third
20   temperature, T_3, determined, in part, by the degree of reaction
completion desired in the vessel. Generally, T_3 ranges from 40
to 95 °C, preferably 60 to 85°C. For a given pH and residence
time, a higher value for T_3 will result in final product
reaction being essentially complete. During circulation, a
25   portion of the mixture will exit the third reaction vessel
through an exit conduit 36. The residence time for the
reactions occurring in the third reaction vessel may be
controlled by varying the circulation rate and size of the
reaction vessel. The residence time of the mixture in the third
30   reaction vessel, R_3, will determine, in part, the completion of
reaction to the final product. Thus, by varying R_3, different
degrees of reaction may be produced. R_3 can range from 2 to 90
minutes. For a given pH_3 and T_3, higher values for R_3 will
result in final product having denser particles.

35   The solution exiting the third reaction vessel 30 through
exit conduit 36 travels to conventional processing equipment
wherein precipitated valve metal pentoxide precursor solids are
recovered from the solution by liquid/solids separation step 40.

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The liquid/solids separation step may be performed in any manner known to the art, such as by filtration. Preferably the liquid/solids separation step is performed by a vacuum or pressure filter.

5   As will be understood by those of ordinary skill in the art, the overall residence time, or the residence time in a reaction vessel may be increased by recycling all, or a portion, of the solution and/or solids exiting each vessel. In particular, an effective way of increasing overall residence

10   time would be to recycle all or a portion of the precipitated solids formed by the process back into the initial vessel. Where recycling is utilized, the effective residence times in each vessel, and/or the effective overall residence time, may be greater than those set forth above for at least a portion of the

15   reacting solution.

After separation of the niobium pentoxide solids, the solids which are not recycled may be washed as shown by solids washing step 50. Solids washing may be accomplished in manners conventional in the art, such as by washing with ammoniated

20   water at a pH of about 9.0.

After washing, the solids are dried, as shown by drying step 60. The resulting product is a hydrated valve metal pentoxide powder having a narrow particle size distribution and a desired particle size. Calcination of the hydrated valve

25   metal pentoxide converts the hydrate to the valve metal pentoxide, e.g. niobium pentoxide, Nb_2O_5 or tantalum pentoxide Ta_2O_5.

Although the addition of materials and reagents has been described with reference to particular portions of the reaction

30   vessels, the materials and reagents may be added to alternative portions of the reaction vessels in order to produce pentoxide products with different characteristics. For example, in the first reaction vessel, the valve metal-containing solution 2, may be added to the outer periphery of the vessel and the

35   ammonia solution added to the center of the vessel. It should further be understood that although the foregoing embodiment utilizes three reaction vessels, the process of the present invention may be conducted utilizing a lesser or greater number

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of reaction vessels depending on the characteristics desired in the final product. Although the foregoing embodiment of the reaction utilizes the mixing and flows as shown, reverse flows may be used as well. Furthermore, a portion of the solids
5 discharged from the third reactor may be recycled to coarsen and densify the particles as desired.

In addition, the present invention provides new valve metal pentoxide precursors, in particular new niobium pentoxide hydrates and new tantalum pentoxide hydrates. The valve metal
10 pentoxide hydrates of the present invention may be processed to produce advantageous valve metal pentoxides. The valve metal pentoxide hydrates of the present invention are characterized by having a line broadened d-value under x-ray analysis at 6 ± 0.3, 3 ± 0.2 and 1.8 ± 0.1 and a fluoride content less than 500 parts
15 per million (ppm), preferably less than 150 ppm. Embodiments of valve metal pentoxide precursors of the present invention may be further characterized as:

(a) niobium pentoxide hydrate having a BET surface area of less than 2 m^2/g, preferably less than 1 m^2/g, more preferably
20 less than 0.5 m^2/g;

(b) niobium pentoxide hydrate having a BET surface area greater than 2 m^2/g, preferably greater than 6 m^2/g, more preferably greater than 50 m^2/g;

(c) tantalum pentoxide hydrate having a BET surface area
25 less than 3 m^2/g, preferably less than 2 m^2/g, more preferably less than 1 m^2/g; and

(d) tantalum pentoxide hydrate having a BET surface area greater than 3 m^2/g, preferably greater than 7 m^2/g, more preferably greater than 11 m^2/g.

30 The valve-metal pentoxide precursors of the present invention may be advantageously produced by the process of the present invention by separating the valve-metal pentoxide precursor prior to converting the precursor to a valve-metal pentoxide.

35 The present invention also provides new valve metal pentoxide powders by calcining the valve metal pentoxide precursors. A first embodiment of such valve metal pentoxide powder may be characterized as low surface area, high density,

substantially spherical agglomeration of calcined niobium
pentoxide particles having a BET surface area less than 2 m^2/g,
preferably less than 1 m^2/g and more preferably less than 0.75
m^2/g or less and a packed bulk density greater than 1.8 g/cc,
5   preferably greater than 1.9, even more preferably greater than 2
g/cc.

     A second embodiment of valve metal pentoxide may be
characterized as high surface area, low bulk density, calcined,
niobium pentoxide particles having a BET surface area greater
10   than 2 m^2/g, preferably greater than 2.5 m^2/g, more preferably
greater than 3 m^2/g, even more preferably greater than 4 m^2/g,
and in some cases yet even more preferably greater than 6 m^2/g,
and a packed bulk density of less than 1.8 g/cc, preferably less
than 1 g/cc and in some cases more preferably less than 0.75
15   g/cc.

     A third embodiment of valve metal pentoxide may be
characterized as low surface area, high bulk density,
substantially spherical agglomerates of calcined, tantalum
pentoxide particles having a BET surface area of less than 3
20   m^2/g, preferably less than 2 m^2/g, more preferably less than 1
m^2/g, and in some cases yet even more preferably less than 0.75
m^2/g or lower, e.g. about 0.4 m^2/g or lower and a packed bulk
density greater than 3 g/cc, preferably greater than 3.5 g/cc,
more preferably greater than 3.8 g/cc and in some cases more
25   preferably greater than 4 g/cc or higher.

     A fourth embodiment of valve metal pentoxide may be
characterized as high surface area, low bulk density, calcined,
tantalum pentoxide particles having a BET surface area greater
than 3 m^2/g, preferably greater than 4 m^2/g, more preferably
30   greater than 5 m^2/g and in some cases greater than 6 m^2/g or even
higher, say at least 7 or even 11 m^2/g and a packed bulk density
less than 3.0 g/cc, preferably less than 2.5 g/cc, more
preferably less than 2 g/cc and in some cases even more
preferably less than 1 g/cc, e.g. about 0.75 g/cc.

35   In the case of low density, high surface area powders, a
substantial number of particles are less than 5 micrometers in
size. For instance although some of the material may be
agglomerated to larger particles, typically 25% or more the

particles, e.g. at least 30% and up to 80%, of the particles are less than 1 micrometer in size. In the case of high density, low surface area powders, most of the particles are agglomerated into large particles typically greater than 5 micrometers.

5   The products of the present invention may be advantageously produced in high purity by the process of the present invention. The fine particles produced by the present invention are highly reactive for use as dopants in various applications, such as electronics, ceramics, and as catalysts. The large dense

10   spherical agglomerated particles have exceptional rheology and can be used for thermite (thermal reduction processes with active metals, i.e., aluminum) or glass applications. The large spherical particles blend well upon mixing with other glass forming ingredients. Furthermore, the large dense particles are

15   not readily airborne in high gas flow streams, thus resulting in high melt efficiencies. Other applications for thermiting, for example, result in the large dense spherical particles giving greater packing factors, thus large thermite batches and greater productivity. In addition, the large, dense particles are not

20   readily airborne during the thermite reaction, thus resulting in greater product recoveries.

      The characterization of the products of this invention for BET surface area, bulk density and particle size can be effected by well known procedures which are commonly used in the art.

25   For instance, BET surface area is determined by measuring a monolayer of nitrogen gas adsorbed on the surface of the particles. Fluoride content is determined by alkaline fusion and separation by volatilization as silicon tetrafluoride from a sulfuric acid solution; fluoride content is determined in a

30   distillate using a specific ion electrode. Particle size can be determined by using laser beam light scattering techniques. While bulk density of agglomerates is determined by weighing a sample of known volume, packed bulk density is determined after mechanical tapping to effect maximum density, e.g. after 5000

35   taps. Morphology of the samples may be determined by visual inspection utilizing scanning electron microscope photographs as necessary.

　　　　The effectiveness and advantages of various aspects and
embodiments of the present invention will be further illustrated
by the following examples in which the valve metal pentoxide
precursor was produced in a continuous process using three
5   reaction vessels substantially as illustrated in Figure 1.
Three 1500 milliliter (ml) beakers were used as the first,
second and third reaction vessels with a nominal working volume
of 1000 ml. The beakers were heated in a double boiler type
set-up where each beaker was surrounded by a container of heat
10   transfer fluid, e.g. water or other heat transfer fluid. In
order to obtain a draft tube set-up, an inner tube with flights
(or baffles) was utilized inside each beaker. Variable speed
impellers were utilized in the bottom of each beaker as
circulation means. Variable speed peristaltic pumps were
15   utilized to control the feed rates of the valve metal-fluoro
solution and ammonia solution to the first two beaker reactors.

EXAMPLE 1

　　　　This example illustrates a process of the present invention
for making relatively high surface area, low density niobium
20   pentoxide precursor and niobium pentoxide (Nb_2O_5) of the present
invention. Reactor bath double boilers filled with deionized
(DI) water were set to 98 °C. A solution of niobium oxyfluoride
at a concentration of 159 g niobium/liter was preheated to about
76 °C and added to the first reactor at 18.5 ml/minute. A
25   solution of 5N ammonia (7.8 wt.%) was added to the first reactor
at 80.5 ml/minute. The reactants were agitated in the first
reactor with a resultant average temperature of 74 °C and pH
8.5. The resulting suspension flowed into the second and third
reactors for further mixing. The reaction was run for 330
30   minutes prior to collection of two liters of suspension which
was filtered, washed and re-slurried with two liters of 5N
ammonia solution at about 80 °C. The resulting slurry was
filtered and washed four more times then filtered to provide a
cake which was dried for sixteen hours at 85 °C, providing 187 g
35   of hydrated niobium pentoxide cake containing 28.4% moisture and
200 ppm fluoride. The hydrated cake was calcined at 900 °C for
four hours providing 97.5 g of niobium pentoxide particles
containing 100 ppm fluoride where 90.9% of the material was

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below 1.5 microns in size (100% was below 24 microns) and high
BET surface area of 2.82 m^2/g. The above and other process
conditions and product characteristics are set forth in Table 1
below.

5   EXAMPLE 2

This example illustrates a process of the present invention
for making a high density, high particle size (low surface area)
niobium pentoxide precursor and niobium pentoxide (Nb$_2$O$_5$) of the
present invention. The procedure of Example 1 was followed
10   except that niobium solution was added to the first reactor at
13.1 ml/min and ammonia solution added at 98.2 ml/min providing
a solution at an average temperature of 61 °C and pH 9.14. The
resulting suspension flowed into the second reactor where an
additional 5.6 ml/minute of niobium oxyfluoride solution was
15   added with agitation. The resultant average temperature and pH
of the second reactor solution were 73 °C and 8.28,
respectively. The resulting second suspension flowed into the
third reactor for further mixing. The reaction was run for 315
minutes, prior to collection of two liters of suspension which
20   was filtered, washed and re-slurried, filtered and calcined as
in Example 1. The uncalcined cake weighed 223.5 g (44.3%
moisture) and contained 460 ppm fluoride. The calcined cake
weighed 85.8 g, containing 180 ppm fluoride and 73.5% of the
material was larger than 96 microns in size. Other process
25   conditions and characteristics are in Table 1.

                               EXAMPLE 3

This example illustrates a process of the present invention
for making a low surface area, high density niobium pentoxide
precursor and niobium pentoxide (Nb$_2$O$_5$) product. The procedure
30   of Example 1 was followed except that niobium solution was added
to the first reactor at 3.5 ml/min and ammonia solution added at
7.8 ml/min providing a solution at an average temperature of 76
°C and pH 7.78. The resulting suspension flowed into the second
reactor where an additional 15.6 ml/minute of ammonia solution
35   was added with agitation. The resultant average temperature and
pH of the second reactor solution were 68 °C and 8.48,
respectively. The resulting second suspension flowed into the

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third reactor for further mixing. The reaction was run for 1100
minutes, prior to collection of two liters of suspension was
collected, filtered, washed and re-slurried, filtered and
calcined as in Example 1. The uncalcined cake weighed 143.1 g
5   (29.07% moisture) and contained 1400 ppm fluoride. The calcined
cake weighed 71.5 g, containing 200 ppm fluoride and had a BET
surface area of 0.5 m^2/g; 77.5% of the material was between 8
and 32 microns in size. Other details and product
characteristics are in Table 1.

10   EXAMPLE 4

     This example illustrates a process of the present invention
for making a high surface area, low density niobium pentoxide
precursor and niobium pentoxide (Nb_2O_5) product. The procedure
of Example 1 was followed except that niobium solution was added
15   to the first reactor at 19 ml/min and ammonia solution added at
34.3 ml/min providing a solution at an average temperature of 80

°C and pH 6.28. The resulting suspension flowed into the second
reactor where an additional 20.9 ml/minute of ammonia solution
was added with agitation. The resulting second suspension at pH
20   8.46 was flowed into the third reactor for further mixing. The
reaction was run for 375 minutes, prior to collection of two
liters of suspension which was filtered, washed and re-slurried,
filtered and calcined as in Example 1. The uncalcined cake
weighed 216.6 g (49.9% moisture) and contained 3600 ppm
25   fluoride. The calcined cake weighed 82.2 g, containing 300 ppm
fluoride and had a BET surface area of 2.18 m^2/g; 30.5% of the
material was smaller than 1 micron in size. Other details and
product characteristics are in Table 1.

                            EXAMPLE 5

30   This example illustrates a process of the present invention
for making a high surface area, low density niobium pentoxide
precursor and niobium pentoxide (Nb_2O_5) product. The procedure
of Example 1 was followed except that niobium solution was added
to the first reactor at 56.5 ml/min and ammonia solution added
35   at 210.4 ml/min providing a solution at an average temperature

of 80 °C and pH 7.72. The resulting suspension flowed into the
second reactor where additional ammonia solution was added with

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agitation to provide the second suspension at pH 8.49 and 70 °C which was flowed into the third reactor for further mixing. Two liters of suspension was collected, filtered, washed and re-slurried, filtered and calcined as in Example 1. The calcined

5   cake contained 100 ppm fluoride and had a packed bulk density of 1.02 g/cc; 28.4% of the material was smaller than 1 micron in size. Other details and product characteristics are in Table 1.

<u>EXAMPLE 6</u>

This example illustrates a process of the present invention

10 for making a high surface area, low density tantalum pentoxide precursor and tantalum pentoxide (Ta_2O_5) product. Reactor bath double boilers were filled with heat transfer oil at 60 °C. A solution of fluorotantalic acid at 80 g tantalum pentoxide/liter and 67 °C and added to a first reactor at 30 ml/minute along

15 with a 5N (7.8 wt.%) ammonia solution at 50 ml/minute. The solutions were mixed in the first reactor to provide first vessel suspension at a temperature of 67 °C and pH 9.01 which overflowed into a second reactor for mixing at 72 °C and pH 8.73. The suspension flowed into the third reactor for mixing

20 at 78 °C and pH 8.42. The reaction was run for 180 minutes prior to collection of two liters of suspension which was filtered, washed and re-slurried with two liters of 5N ammonia solution at 85 °C. The resulting slurry was filtered, washed four additional times and filtered to provide a wet cake which

25 was dried for six hours at 100 °C. The wet cake weighed 121.7 g (2.43% moisture) and contained 50 ppm fluoride and was calcined at 900 °C for one hour to provide 108 g of dry, calcined cake containing less than 50 ppm fluoride, having a BET surface area of 6.7 m^2/g and a packed density of 1.81 g/cc; 78.6% of the

30 calcined cake was smaller than 1 micron in size. Other process conditions and product characteristics are shown in Table 1.

<u>EXAMPLE 7</u>

This example illustrates the preparation of a low density tantalum pentoxide and precursor. The procedure of Example 6

35 was followed except that fluorotantalic acid solution at 66 °C was added to the first reactor at 30 ml/min and ammonia solution added at 35 ml/min providing a solution at an average

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temperature of 74 °C and pH 8.42. The resulting suspension

flowed into the second reactor for additional mixing at 77 °C and

pH 8.2 and then to a third reactor for mixing at 82 °C and pH

8.0. The reaction was run for 375 minutes prior to collection of

5   two liters of suspension.   232 g of wet cake (11.9% moisture)

contained 310 ppm fluoride. Other details and product

characteristics are in Table 1.

<div align="center">EXAMPLE 8</div>

This example illustrates the production of high surface

10   area, low density tantalum pentoxide and precursor. The

procedure of Example 6 was followed except that the

fluorotantalic acid solution at 73 °C was added at 25 ml/min and

the ammonia solution was added at 25 ml/min to provide a first

suspension at 74 °C and pH 8.42. The first suspension was

15   flowed into a second reactor for further mixing with an

additional 50 ml/min of the ammonia solution to provide a second

suspension at 60 °C and pH 9.5 which was flowed in to a third

reactor for further mixing at 71 °C and pH 9.08. The reaction

was run for 255 minutes, prior to collection of six liters of

20   suspension. The wet cake contained less than 50 ppm fluoride.

The calcined cake had a BET surface area of 4.96 m^2/g and a

packed density of 2.96 g/cc.

20

EXAMPLE 9

This example illustrates the preparation of a low surface area, high density agglomerated tantalum pentoxide and precursor essentially following the procedure of Example 6 except that a

5   fluorotantalic acid solution (87 g/l Ta_2O_5 and containing 0.7% EDTA) was added to the first reactor at a fixed rate and mixed with a 30% ammonia solution at a rate adjusted to provide a pH of 7.49. A first suspension at 64 °C was flowed to a second reactor and mixed with additional ammonia solution to provide a

10   suspension at 61.8 °C and pH 8.55 which was flowed to a third reactor for further mixing at 63.5 °C and pH 8.14. The reaction was run for 240 minutes prior to collection of suspension which was filtered to provide a wet cake containing 90 ppm fluoride. the wet cake was calcined at 1050 °C for 1 hour providing a

15   calcined powder with a BET surface area of 1.01 m^2/g and a packed density of 3.98 g/cc. Other process conditions and product characteristics are shown in Table 1.

EXAMPLE 10

This example illustrates the preparation of a high surface

20   area, low density tantalum pentoxide and precursor by essentially following the procedure of Example 9 except that the first suspension was at 55.6 °C and pH 9.51. The second suspension was at 53.3 °C and pH 9.06 and the third suspension was at 55 °C and pH 8.84. The reaction was run for 240 minutes

25   prior to collection of suspension. The wet cake was calcined at 900 °C providing powder having a BET surface area of 5.17 m^2/g and a packed density of 1.6 g/cc.

The results set forth in Table 1 indicate that a preferred process of the present invention may be utilized to produce a

30   wide variety of niobium pentoxide precursors, niobium pentoxide (Nb_2O_5) powder products, tantalum pentoxide precursors and tantalum pentoxide (Ta_2O_5) powder products which fall within the scope of the present invention.

Table 1

Example	1	2	3	4	5
Compound	Nb_2O_5	Nb_2O_5	Nb_2O_5	Nb_2O_5	Nb_2O_5
pH Rx.1	8.52	9.14	7.78	6.28	7.72
pH Rx.2	8.39	8.28	8.48	8.46	8.49
Total Residence Time (min)	31	27	115	42	12
Temperature °C, Rx.1	74	61	76	80	80
Rx. Split Rx.1%:Rx.2%	100:0	70:30	33:67	62:38	76:67
(ppm F) Filtered	21500	80000	64000	13500	13500
Washed	260	460	1400	3600	2350
Calcined	100	100	200	300	100
Settled Volume (ml)	240	270	20	320	90
Freefall Density (g/cc)	1.24	1.57	1.51	1.23	0.74
Packed Density (g/cc)	1.71	1.84	2.06	1.62	1.02
Uncalcined Percent Moisture	28.4	44.3	29.1	49.9	35.8
% < 1 μm	70.3	15.3	1.4	30.5	28.4
90% < __ μm	1.5	150	27	96	20
Surface Area (m^2/g)	2.82	--	0.5	2.18	--

Rx.1 = Reaction in first reaction vessel

Rx.2 = Reaction in second reaction vessel

% < 1 μm = percentage of product smaller than 1 micrometer

90% < μm = the particle size where 90% of particles are less
        than or equal to the size

Table 1 (continued)

Example	6	7	8	9	10
Compound	Ta_2O_5	Ta_2O_5	Ta_2O_5	Ta_2O_5	Ta_2O_5
pH Rx.1	9.01	8.42	7.53	7.5	9.51
pH Rx.2	8.73	8.2	9.5	8.5	9.06
Total Residence Time (min)	38	46	33	120	120
Temperature °C, Rx.1	67	74	83	64	56
Rx. Split Rx.1%:Rx.2%	100:0	100:0	26:74	52:48	100:0
(ppm F) Filtered	54000	75000	7500	32000	96000
Washed	50	310	<50	90	130
Calcined	<50	200	<50	120	70
Settled Volume (ml)	155	120	15	30	176
Freefall Density (g/cc)	1.36	1.32	2.35	2.65	0.98
Packed Density (g/cc)	1.81	1.77	2.96	3.98	1.60
Uncalcined Percent Moisture	11.3	11.9	16.3	10	35
% < 1 μm	78.6	10.6	5.8	0	2.7
90% < __ μm	5	5	55	35	3.5
Surface Area (m^2/g)	6.7	--	4.96	1.01	5.17

Rx.1 = Reaction in first reaction vessel

Rx.2 = Reaction in second reaction vessel

% < 1 μm = percentage of product smaller than 1 micrometer

90% < μm = the particle size where 90% of particles are less
         than or equal to the size

The results shown in Table 1 also illustrate that the rate
of precipitation and residence time in the reactors for particle
ripening can increase product density. Scanning electron
photomicrographs of material precipitated near the isoelectric
point of 7.7 for Nb_2O_5 with a 115 minute and a 12 minute
residence time are shown in Figures 2 and 3, respectively.
Figures 2a, 2b, 2c and 2d are scanning electron photomicrographs
of the Nb_2O_5 produced in Example 3, at different magnifications.
Figures 3a, 3b, 3c and 3d are scanning electron
photomicrographs of the Nb_2O_5 produced in Example 5, at different
magnifications. Figures 4a, 4b, 4c and 4d are scanning electron
photomicrographs of the Ta_2O_5 produced in Example 9, at different
magnifications. Figures 5a, 5b, 5c and 5d are scanning electron
photomicrographs of the Ta_2O_5 produced in Example 10, at
different magnifications. The "a" micrograph shows the product
powder at a 100x magnification; "b", at 500x; "c", at 1,000x;
and "d", at 10,000x.

With reference to Figures 2a-2d and 3a-3d, the low density,
high surface area particles produced in Example 5 at a 12 minute
residence time (shown in Figures 3a-3d) are visually
significantly less dense than the particles produced in Example
3 at a 115 minute residence time (shown in Figures 2a-2d). The
very closely packed crystallites shown in Figures 2a-2d also
exhibit crystal intergrowth and densification as seen in the
photomicrographs. Figures 5a-5d show the fine calcined
particles of Ta_2O_5 produced at pH 9.5 with a 2 hour residence
time while Figures 4a-4d show dense particles of Ta_2O_5 produced
at a pH of 7.5 and a 120 minute residence time. These
photomicrographs illustrate a range of particles which can be
produced by the process of the present invention.

The examples discussed herein further illustrate that the
process of the present invention produces ammonium fluoride and
microcrystalline valve metal pentoxide hydrates with a readily
defined line broadened x-ray diffraction pattern and the
calcined pentoxide analog.

The Zeta potential of the pentoxide hydrate in the presence
of ammonium fluoride is negative at pH's of 8 or greater and
positive at pH's of 6 or less as shown by Figure 6. The

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isoelectric point or point of zero charge is in the range of pH
7-8. Precipitation at the isoelectric point allows
agglomeration and formation of dense substantially spherical
particles. This feature of the process of the present invention
5 allows the control of precipitated particle sizes. At pH's
above and below the isoelectric point, the charged particles
repel one another preventing agglomeration and fine particles
are precipitated.

It should be clearly understood that the forms of the
10 present invention herein described are illustrative only and are
not intended to limit the scope of the invention.

CLAIMS

1. A process for producing a valve metal oxide compound comprising:

        mixing in a first vessel an aqueous mixture of an
5   ammonia solution and a fluoride-containing solution
        comprising fluorotantalic acid or niobium oxyfluoride at
        temperature, pH and residence time conditions to initiate
        precipitation of hydrated valve metal pentoxide, wherein
        said valve metal is tantalum or niobium;
10   transferring said mixture into at least one other
        vessel for mixing at the same or different temperature, pH
        and residence time conditions to continue further
        precipitation of hydrated valve metal pentoxide.

2. The process of claim 1 further comprising transferring said
15 mixture to at least a third vessel and mixing at the same or
    different temperature, pH and residence time conditions to
    continue further precipitation of hydrated valve metal
    pentoxide.

3. The process according to claim 2 wherein additional ammonia
20 solution or fluoride-containing solution is added to said second
    vessel or to said third vessel or both.

4. The process of claim 3 wherein said hydrated valve metal
    pentoxide is converted to valve metal pentoxide by calcining at
    a temperature greater than at least 790 °C to provide tantalum
25 pentoxide or at a temperature greater than at least 650 °C to
    provide niobium pentoxide.

5. Niobium pentoxide powder characterized as (a) having a BET
    surface area less than 2 m^2/g and a packed bulk density greater
    than 1.8 g/cc or (b) having a BET surface area of greater than 2
30 m^2/g and a packed bulk density less than 1.8 g/cc.

6. Tantalum pentoxide powder characterized as (a) having a BET
    surface area less than 3 m^2/g and a packed bulk density of
    greater than 3.0 g/cc or (b) having a BET surface area greater
    than 3 m^2/g and a packed bulk density less than 3.0 g/cc.

35 7. A valve metal pentoxide precursor characterized by a line
    broadened d-values under x-ray analysis of 6 ± 0.3, 3 ± 0.2 and
    1.8 ± 0.1, wherein the valve metal is niobium or tantalum and
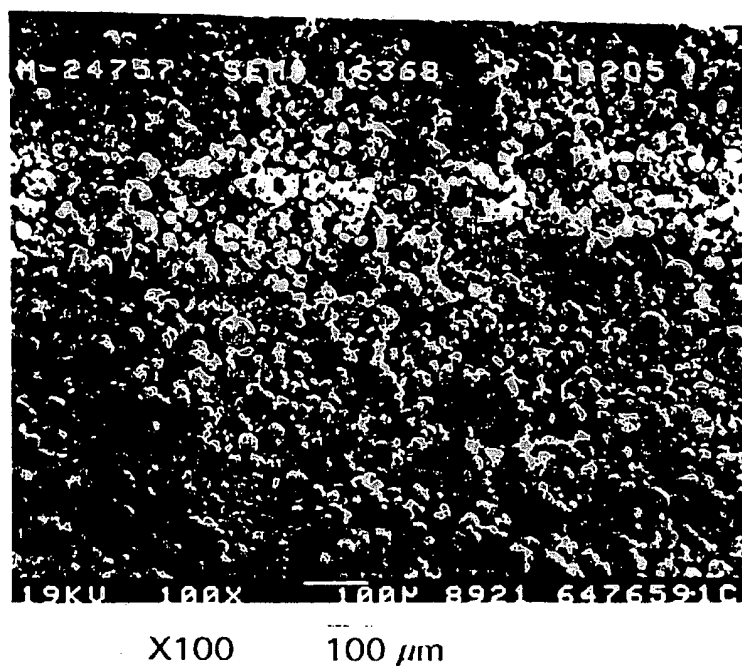   the precursor has a fluoride content less than 500 ppm.

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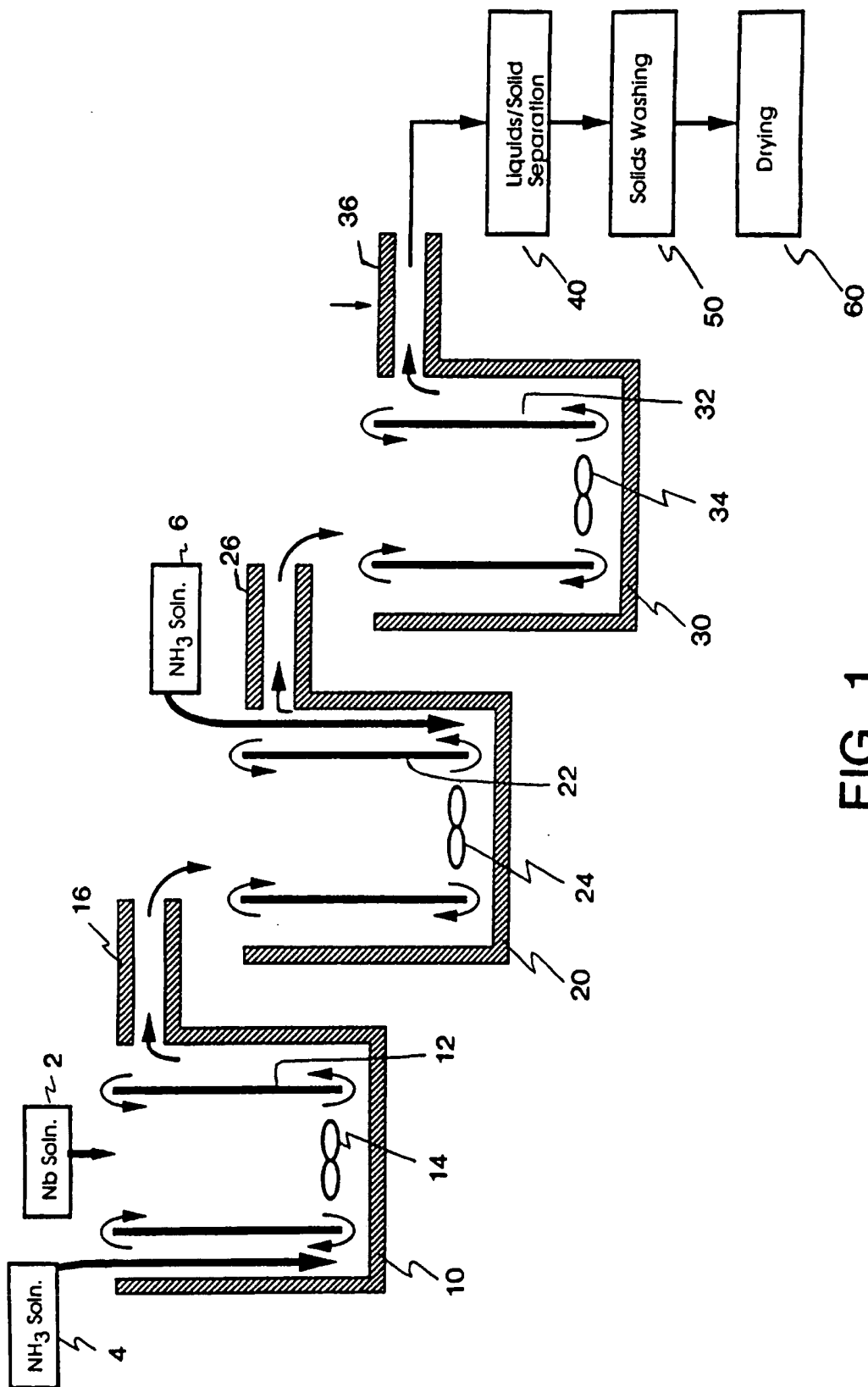
FIG. 1

X100   100 μm
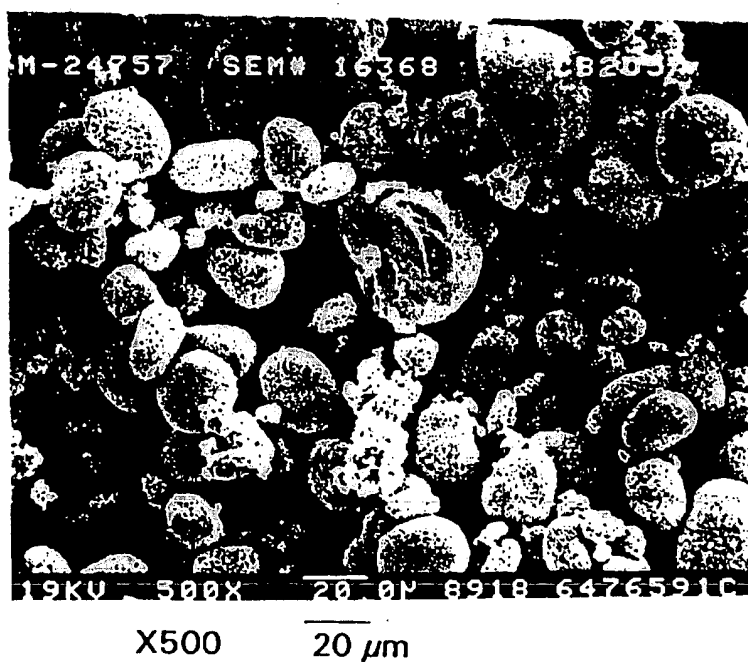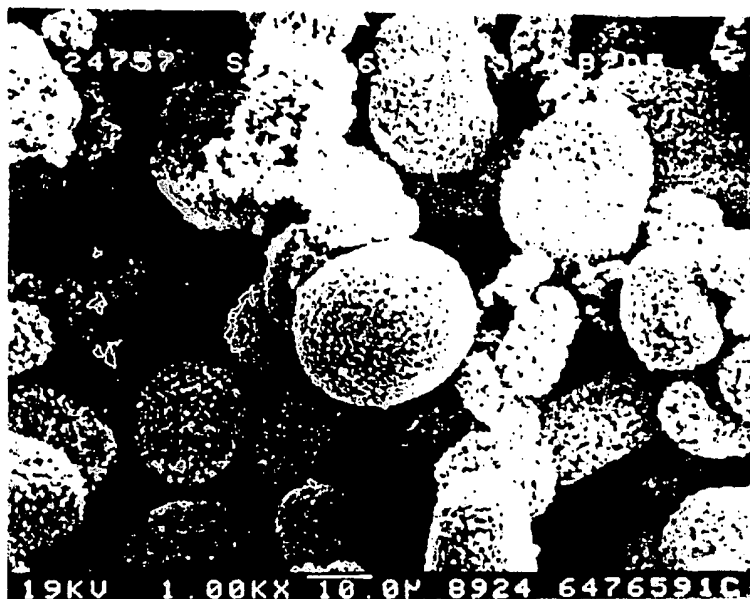
FIG. 2A

X500   20 μm

FIG. 2B

X1,000   10 μm

FIG. 2C

X10,000   1 μm

FIG. 2D

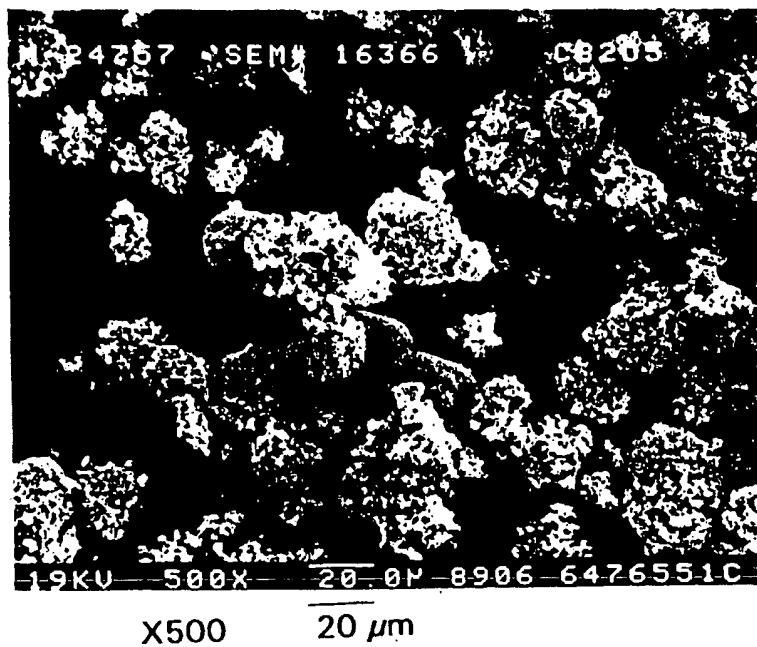X100   100 μm
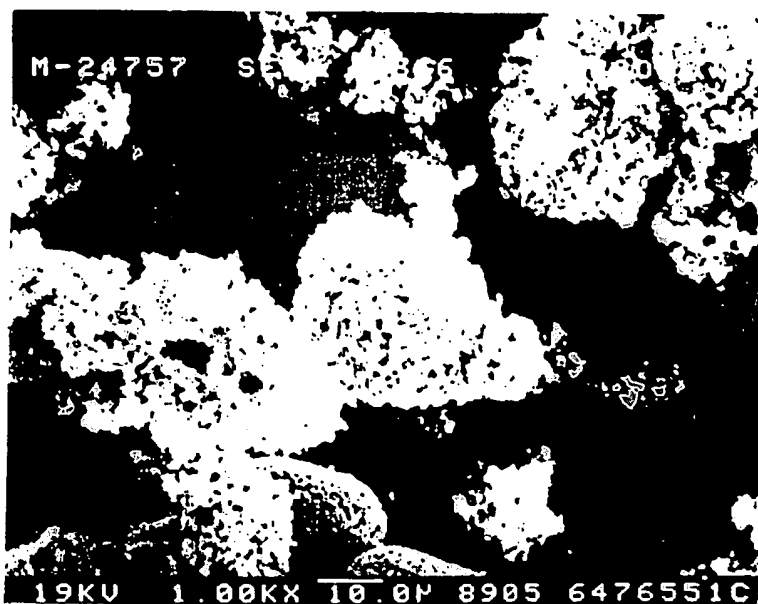
FIG. 3A

X500   20 μm

FIG. 3B

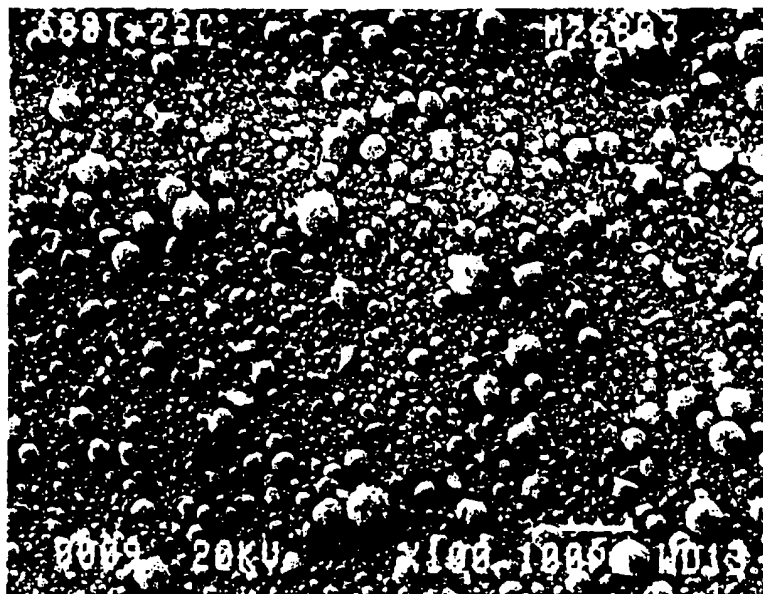5 / 9
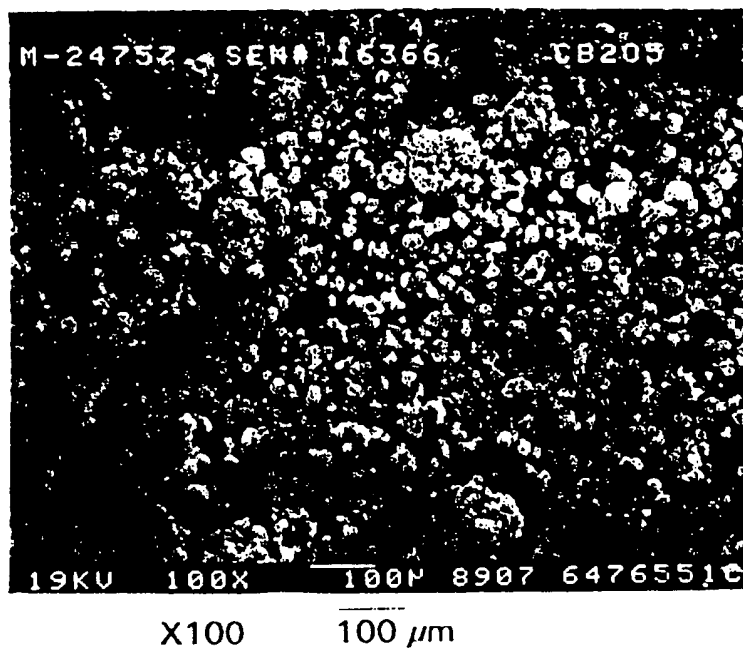
X1,000   10 μm

FIG. 3C

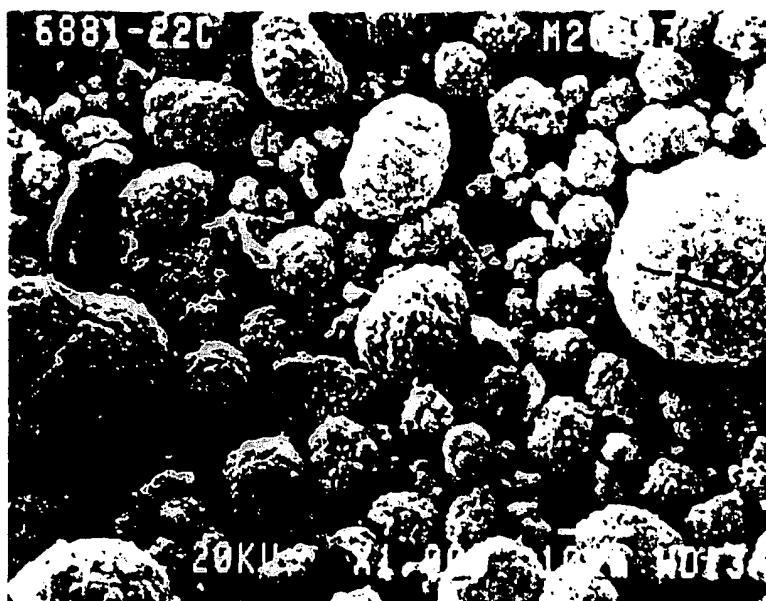X10,000   1 μm
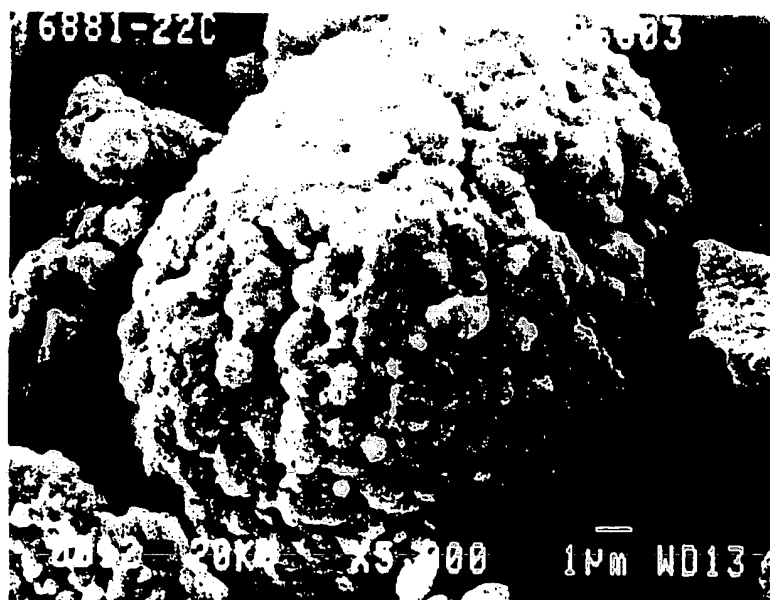
FIG. 3D

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FIG. 4A

FIG. 4B

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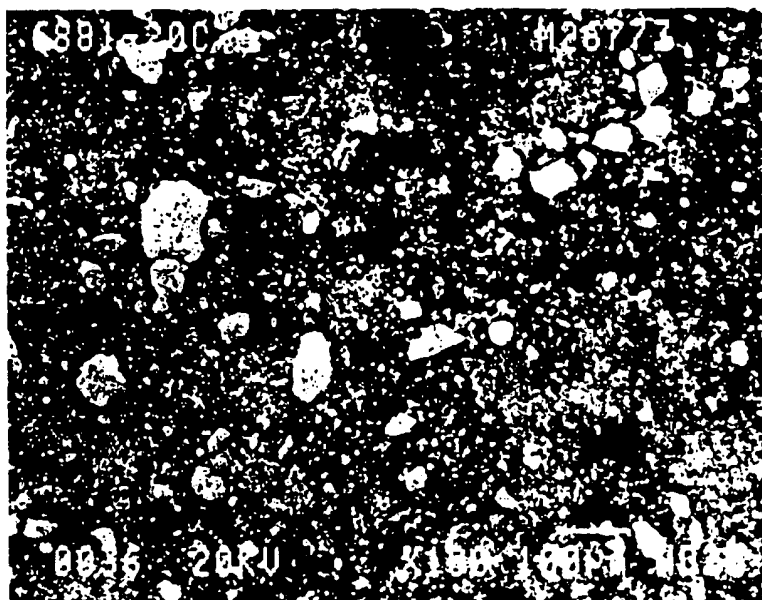FIG. 4C

FIG. 4D

FIG. 5A
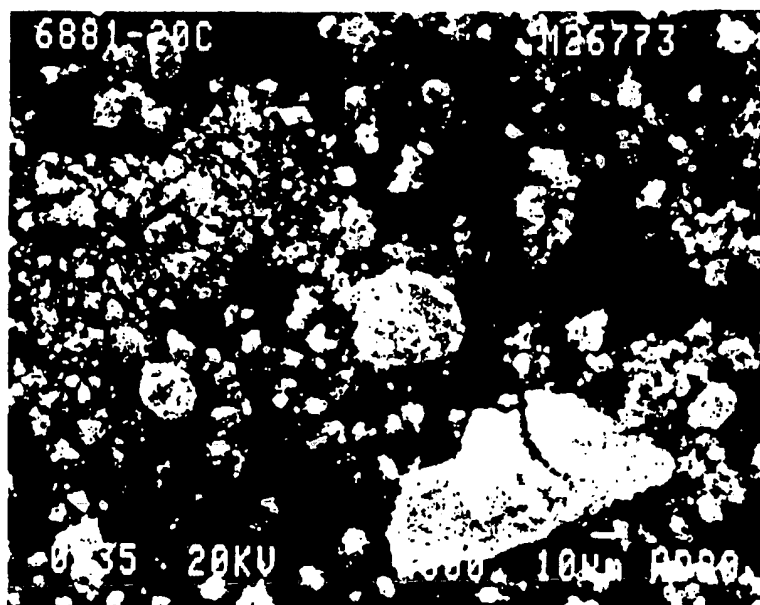
FIG. 5B
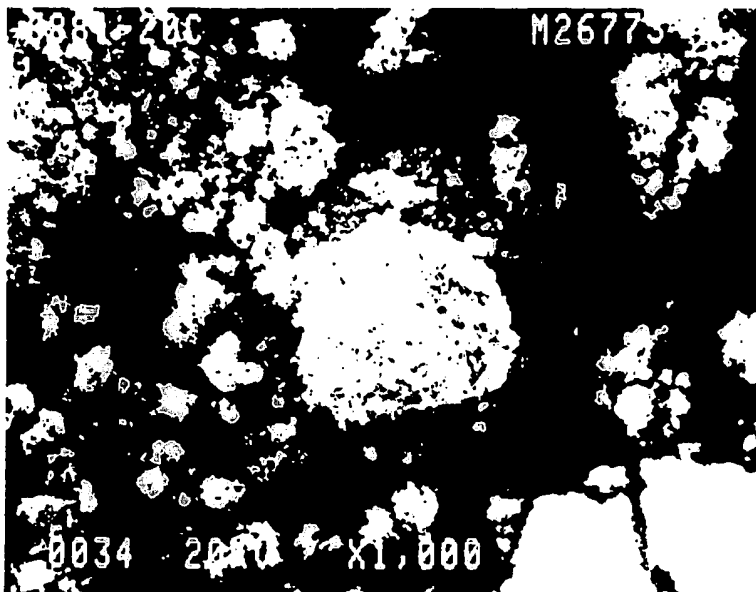
FIG. 5C

FIG. 5D

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C01G33/00   C01G35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,34 28 788 (BAUER GUENTER J;ECKERT JOACHIM DR) 4 April 1985 see page 5, line 16 - line 30 see page 8, line 4 - line 13	1
A	see examples 1,2 -----	4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 January 1997	2 3. 01. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	LIBBERECHT, E

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3428788	04-04-85	NONE	